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SEPARATION OF ZINC IONS FROM AQUEOUS SOLUTIONS USING MODIFIED SILICA IMPREGNATED WITH CYANEX 272

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ABSTRACT

Di-2,4,4-trimethylpentyl phosphinic acid (CYANEX 272) was immobilized on a silica surface after it was treated with dichlorodimethylsilane and chlorotripropylsilane. The resulting adsorbent prepared showed an excellent selectivity for zinc ion in aqueous solutions and was stable under acidic conditions. Change in surface and pore structure were investigated by means of FT-IR and BET, respectively. The metal ion adsorption capacity order of the resulting adsorbent (silica powder impregnated with CYANEX 272 after silanization of dichlorodimethylsilane, SPDC) was $\text{Zn}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$ in the pH range of 2–5. Fixed bed tests were conducted in order to evaluate the efficiency of removal of metal ions using the SPDC, and a breakthrough curve was obtained for the zinc solution. The adsorbed zinc ions could be recovered by treatment with 0.1 M HCl, which permits cyclic use after regeneration.

Key Words: CYANEX 272; Cyclic use; Selectivity

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INTRODUCTION

Water pollution, as a result of the release of heavy metal ions from industrial wastewater, causes serious environmental problems. Waste streams from industries contain a variety of metal ions, including copper, nickel, zinc, cobalt, chromium (+6), lead, mercury, and cadmium (1). Several adsorptive materials have been applied to the removal of heavy metals from aqueous solution, including metal oxides, charcoal, zeolites, and clays (2). However, an inherent disadvantage of these materials is their low selectivity for a specific heavy metal. Silica impregnated with ion-chelating agents has been examined for removing heavy metals from dilute metal waste-streams (3–8). Interest stems from its resistance to swelling, good selectivity, rapid sorption of metal ions, and the low loss of ion-chelating agents compared to solvent extraction, as well as its good mechanical stability (3). In addition, this adsorption process has advantages, such as simple process and sludge-free operation. Although the sorption capacities of such modified silica preparations is relatively small, it can be used efficiently in the treatment of waste streams that contain small quantities of heavy-metal ions.

Ion-chelating organic molecules are usually chemically bonded to the silica surface by means of silanization procedures (9,10). However, some of ion-chelating agents may not contain a reactive functional group that is suitable for chemical bonding with a silanized inorganic surface. In this case, physical adsorption of organic chelating agents on the support is an alternative possibility. Physical adsorption can be achieved through interactions, such as van der Waals forces, between the organic agent and a hydrophobic surface (3,11–13). Di-2,4,4-trimethylpentyl phosphinic acid (CYANEX 272) has been examined as a heavy metal extractant for the removal of zinc, cobalt, chromium, cadmium, iron, and nickel (14–21). In this study, CYANEX 272 was attached to the silica surface through silanization. The characteristics of the prepared adsorbents with respect to stability and zinc ion adsorption are reported.

EXPERIMENTAL

Materials

A silica powder (Aldrich Chemical Co., WI) was used as a support to prepare ceramic materials having a selective affinity for zinc ion. The properties are as follows: surface area of 300 m²/g, diameter between 0.149 and 0.074 mm, average pore diameter of 15.0 nm, pore volume of 1.15 mL/g, and bulk density of 0.34 g/mL.



Dichlorodimethylsilane (Aldrich Chemical Co., WI) and chlorotripropylsilane (Aldrich Chemical Co.) were used for the surface treatment of silica supports. Di-2,4,4-trimethylpentyl phosphinic acid (Henkel Co., USA) was used as a chelating agent without further purification. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Junsei Chemical Co., Japan) was used to prepare solutions of zinc ions. Other solutions containing metal ions (Ni^{2+} , Co^{2+} , Cu^{2+} , Cd^{2+}) were also prepared from metal nitrate salts (Junsei Chemical Co., Japan). Potassium chloride (Aldrich, WI), potassium hydrogen phthalate (SIGMA, MO) were used to prepare buffer solutions. Deionized water, 0.1, 1.0 M HCl, and 0.01 M NaOH were used for the desorption of metal ions attached to the modified silica. All reagents were of analytical grade.

Preparation of Ceramic Materials Having a Selective Affinity for Zinc Ion

Ceramic materials having a selective affinity for zinc ion were prepared as follows: Silica powders were dried initially to remove moisture from their surface. Dried silica (hereafter referred to as SP) was prepared after drying at 100°C in an oven for 3 hr.

Ten grams of SP sample was shaken for 16 hr with 40 g of either chlorotripropylsilane or dichlorodimethylsilane. The silanized silicas were dried under vacuum at 30 mmHg, 100°C, to remove unreacted silane. The dried silica was then washed with deionized water to remove residual HCl and dried under vacuum at 30 mmHg, 100°C. The silicas, which had been silanized with chlorotripropylsilane and dichlorodimethylsilane, were designated as SPC and SPD, respectively.

For impregnation with CYANEX 272, 40 g of a 20 wt% CYANEX 272 solution, mixed with 80 wt% toluene, was added to each flask containing 10 g of silanized silicas (SPC, SPD), and the flasks were shaken gently on a rotating shaker for 2 hr. The impregnated silica was separated from the solution, air dried at atmosphere and then at 110°C to completely remove the toluene. The impregnated silicas that had been silanized with chlorotripropylsilane and dichlorodimethylsilane were designated as SPCC and SPDC, respectively.

Adsorption and Regeneration

The stability of the prepared adsorbents (SPCC and SPDC) was experimentally measured under both acidic and basic conditions to determine which sample and which condition is best for use in a continuous adsorption/regeneration process. For application to practical processes, the



adsorbents should be stable and should not be altered by the regeneration procedure. Therefore, it becomes really necessary to have specific knowledge of the conditions used in their regeneration. This was tested under the extreme conditions. Both adsorbents were shaken in two acidic solutions (0.1 and 1.0 *M* HCl), an alkaline solution (0.01 *M* NaOH) and neutralized water for 7 days, respectively. After this treatment and subsequent drying, a 0.2 g treated sample of SPCC or SPDC was suspended in 25 mL of 5 mmol/L zinc solutions for 24 hr, in order to determine which adsorbent was more effective for further experiments. The amounts of zinc ion adsorbed on the regenerated adsorbents were determined by atomic absorption spectrometer, and compared with those on the non-treated adsorbents.

After a superior adsorbent and conditions for its regeneration were identified, the affinity for several metals (Cd^{2+} , Co^{2+} , Cu^{2+} , Ni^{2+} , and Zn^{2+}) and the effect of pH on their adsorption were examined for SPDC. A 0.2 g sample of SPDC was shaken in an aqueous solution of each metal at a concentration of 5 mmol/L and equilibrated for 24 hr. For this experiment, buffer solutions were used to maintain the solution at a constant pH in the batch reaction systems, and the solution pH was controlled at below 5 to prevent hydroxide precipitation (0.2 *M* KCl and 0.2 *M* HCl for pH 2; 0.1 *M* potassium hydrogen phthalate and 0.1 *M* HCl for pH 3, 4; 0.1 *M* potassium hydrogen phthalate, and 0.1 *M* NaOH for pH 5).

The break-through behavior of zinc ion was obtained by passing a zinc solution (1 mmol/L) through a packed-column (ID 16 mm) loaded with 5 g of the SPDC. The pH of the zinc solution was fixed at 4.3, based on the results of the selectivity experiment, and the flow-rates were maintained at 5 mL/min. The elution experiment was conducted after the SPDC was nearly saturated with zinc ions. A 0.1 *M* HCl solution was fed to the reactor at a rate of 5 mL/min in order to elute the zinc ions from the SPDC. The Zn^{2+} -adsorbed SPDC is referred to as SPDCM.

The selective removal of zinc ions from cobalt ions using the SPDC sample also was investigated in both the batch and the continuous reactor. In the batch system, competitive adsorption experiments were carried out using aqueous solutions containing Zn^{2+} and Co^{2+} . In this experiment, 0.2 g of SPDC was added to 25 mL of a binary mixture containing equimolar amounts (5 mmol/L) of the metal ions, followed by equilibration for 24 hr. In the continuous system, a mixture solution of zinc and cobalt (1 mmol/L) was passed through a packed-column (ID = 16 mm) that has been loaded with 5 g of the adsorbent (SPDC). The flow-rate was about 5 mL/min, and the pH of the feed solution was adjusted to approximately 4.0 with a 0.1 *M* HCl solution.

The CYANEX 272–zinc complex which is formed at the SPDC surface can be regenerated into CYANEX 272 and free zinc ion at low pH. This is achieved by suppressing the forward reaction rate and accelerating the backward reaction rate by increasing the H^+ concentration of the solution. In order to investigate the effect of the repeated use on SPDC capacity, successive adsorption and elution rate data for SPDC were obtained using a packed-column

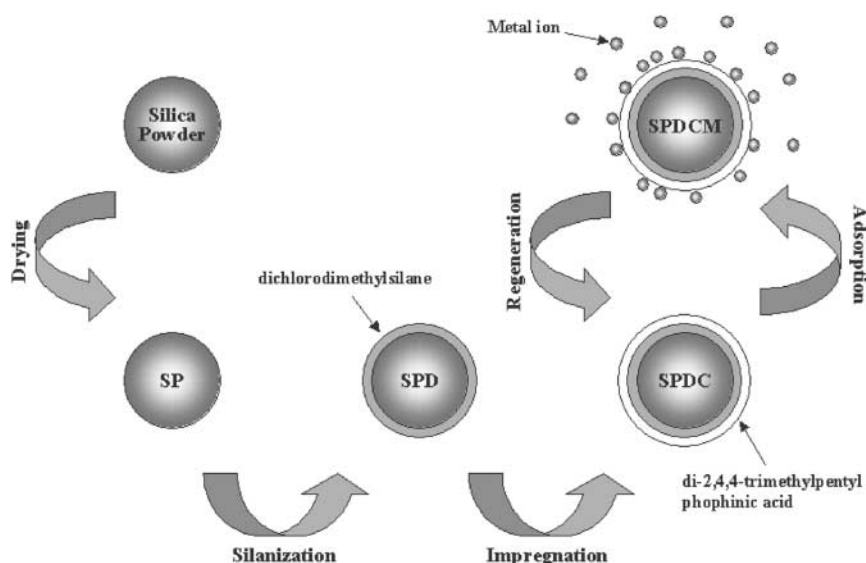


reactor (ID = 11 mm) loaded with 0.5 g of SPDC. Zinc solution (200 mL, 2 mmol/L, pH 4) was fed to the reactor at a rate of 5 mL/min for 2 hr. Then, 100 mL of a 0.1 M HCl solution was fed to the reactor for 3 hr at the same rate, in order to desorb the zinc ions from the adsorbents. This operation was repeated for 17 adsorption and elution cycles. Adsorption and desorption operation times were 2 and 3 hr, respectively.

The designation of all the samples is shown in Sch. 1 with abbreviations.

Characterization

Four characterization methods were performed for the samples (SP, SPD, SPDC, and SPDCM) at each preparation and treatment step. An FT-IR (Jasco, FT/IR-200, Jasco Inc., MD) was used to determine the nature of the bonding of organics to the surface and a CHN Corder (Yanaco, MT-2, Yanaco Co., Japan) was used for elemental analysis to determine quantitatively the amount of organic molecules in each substrate. The changes in surface area, average diameter, and pore volume were examined by means of BET (ASAP 2010, Micromeritics Instrument Co., GA). The concentrations of metal ions in the solutions were determined using an Atomic Absorption Spectrometer (Model 3110, Perkin-Elmer, MA).



Scheme 1. Schematic showing preparation, adsorption and regeneration of silicas.



RESULTS AND DISCUSSION

Immobilization of Di-2,4,4-Trimethylpentyl Phosphinic Acid

The hydrophilicity of the OH groups on the silica surface prevents chelating agents from adsorbing to the SP. In order to introduce hydrophobicity to the surface, the SP was treated with silane derivatives. The silanized porous silica should be susceptible to impregnation at the level of the minute pores of SP. Chlorotripropylsilane and dichlorodimethylsilane, which have short hydrocarbon chains, were selected for this purpose.

Figure 1 shows the FT-IR data for the SP (a), SPD (b), and SPDC (c). A broad peak was observed near 3500 cm^{-1} in the SP. This is due to the O-H functional groups on the silica surface. The O-H peak disappeared after the reaction of dichlorodimethylsilane with the silica. The C-H peak near 3000 cm^{-1} in the SPD provides evidence for the presence of dichlorodimethylsilane on the silica surface. The peak corresponding to a methyl group was increased after impregnation, indicating the attachment of CYANEX 272 on the surface. Since the methyl groups on the silanized silica would not be expected to form chemical bonds with the CYANEX 272 molecules, it is

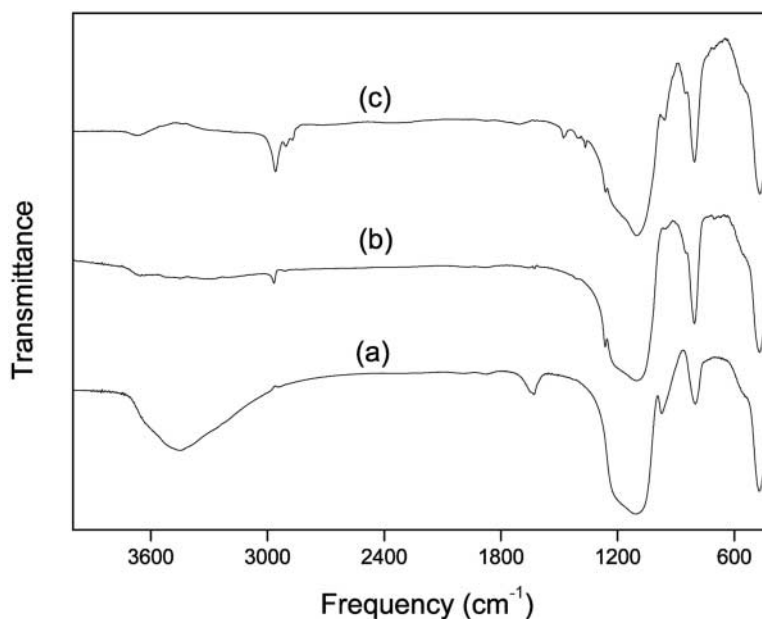


Figure 1. FT-IR data for (a) SP, (b) SPD, and (c) SPDC.



Table 1. BET Results for Each Step

| Properties | SP | SPD | SPDC | SPDCM |
|----------------------------------|------|------|------|-------|
| Surface area (m ² /g) | 293 | 133 | 53.7 | 46.7 |
| Average pore diameter (nm) | 14.7 | 15.1 | 16.6 | 15.3 |
| Pore volume (cm ³ /g) | 1.16 | 0.64 | 0.27 | 0.22 |

likely that the CYANEX 272 binds to hydrocarbon chains on the silanized surface by non-covalent bonding such as van der Waals interactions. In this case, the binding force is probably weaker than that of chemical adsorption. More study is needed to confirm the bonding structure between CYANEX 272 and silanized silica.

The surface area, average pore diameter, and pore volume of SP, SPD, SPDC, and SPDCM were analyzed with BET. As SP was successively treated, the surface area and pore volume decreased while the average pore diameter remained almost constant (Table 1). However, a significant pore volume was retained after silanization, permitting the impregnation of CYANEX 272. The cumulative pore-volume change with pore size [Fig. 2(a)] confirms that the fraction of small pores decreased on grafting with organics. In addition, the extent of decrease in pore volume by the adsorption of zinc ions was relatively small. This implies that relatively small pores were blocked when the surface is treated with dichlorodimethylsilane or CYANEX 272. The N₂ adsorption-desorption isotherms are shown in Fig. 2(b). This figure also shows that as the organic grafting progressed, the volume of N₂ adsorbed decreased.

Stability

The stabilities of SPDC and SPCC under a variety of aqueous conditions were investigated. Table 2 shows that the carbon percentage of carbon in the adsorbents remained the same after treatment with acidic and neutralized solutions while it was reduced after treatment with an alkaline solution. Moreover, the elemental analysis data for the treated adsorbents were in good agreement with the zinc adsorption experiments. For example, in the cases of SPDC, exposure to 1.0, 0.1 M HCl, and neutralized water resulted in no change in capacity while treatment with a 0.01 M NaOH solution caused a significant reduction in capacity: 0.31, 0.30, 0.29, 0.30, 0.21 mmol/g for SPDC treated with 1.0, 0.1 M HCl, neutralized water, and 0.01 M NaOH, respectively. It appears that NaOH causes CYANEX 272 to be detached from the surface, and



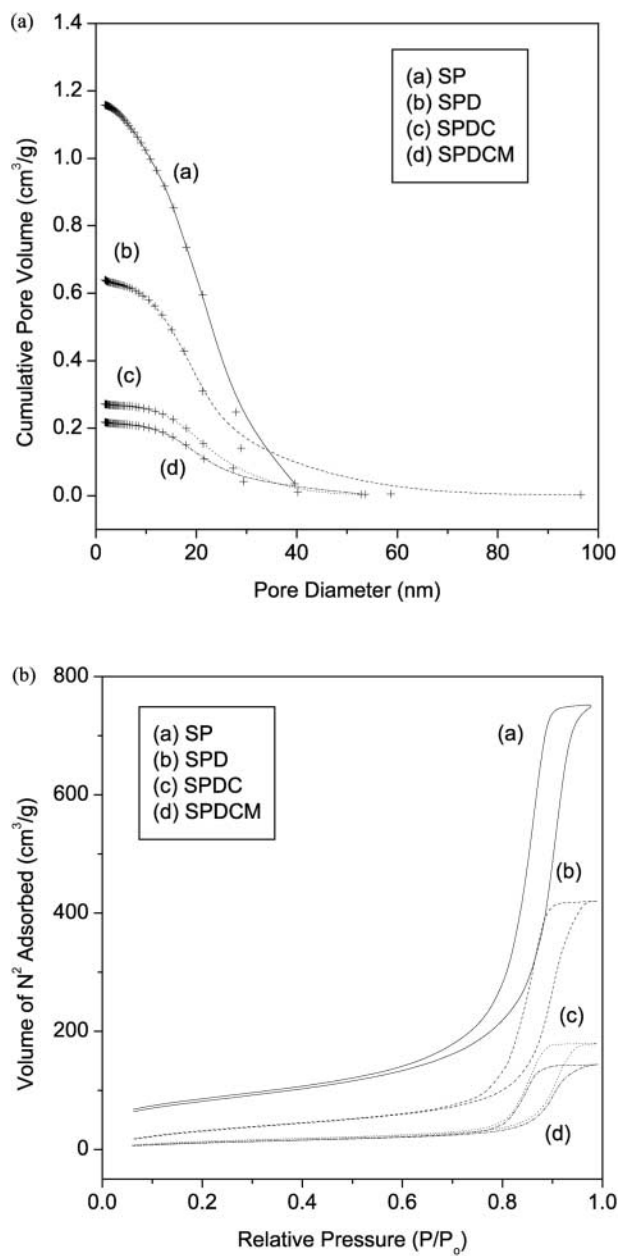


Figure 2. BET data for SP, SPD, SPDC, and SPDCM: (a) cumulative pore volume; and (b) N_2 adsorption-desorption isotherm.



Table 2. Percentage of Carbon in SPDC and SPCC Before and After Treatment

| | SPDC (C%) | SPCC (C%) |
|--------------------------------|-----------|-----------|
| Untreated | 21.6 | 22.7 |
| Treated with neutralized water | 22.4 | 23.4 |
| Treated with 0.1 M HCl | 22.4 | 23.6 |
| Treated with 1.0 M HCl | 22.5 | 23.0 |
| Treated with 0.01 M NaOH | 17.0 | 18.5 |

that the reduction in capacity is due to the loss of CYANEX 272 molecules from the surface. It is clear that CYANEX 272-adsorbed-adsorbents are stable in acidic or neutralized condition, and that they can be regenerated under these conditions.

Two samples (SPDC and SPCC) were compared for their adsorption capacity for zinc ion. The removal capacities for zinc ion for the SPDC and SPCC samples were around 0.31 and 0.26 mmol/g, respectively. From these results, it is inferred that SPDC is a more effective adsorbent, based on stability and capacity, and further experiments are now being concentrated on SPDC.

Selectivity

Figure 3 shows the adsorption capacity of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , and Cd^{2+} in a single solution as a function of solution pH. The order of adsorption capacity for the five tested metal ions was $\text{Zn}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$, i.e., the efficiency for the removal of zinc ions showed the highest value, of the five metal ions studied. The capacity for zinc adsorption increased dramatically with solution pH over the range of 2–5. At pH 4, cobalt and copper ions were adsorbed only slightly, and the adsorption capacities of the two ions increased at pH 5. The slight amount of cadmium ions was adsorbed only at pH 5, and the removal of nickel ions was negligible in the given pH range. The results are in good agreement with the pH dependence of CYANEX 272 for each metal ion reported elsewhere (21).

Break-Through and Elution Curve for Zinc

The result of the break-through experiment (Fig. 4) showed that about 50 bed volumes of feed solution could be passed through the adsorbent with below



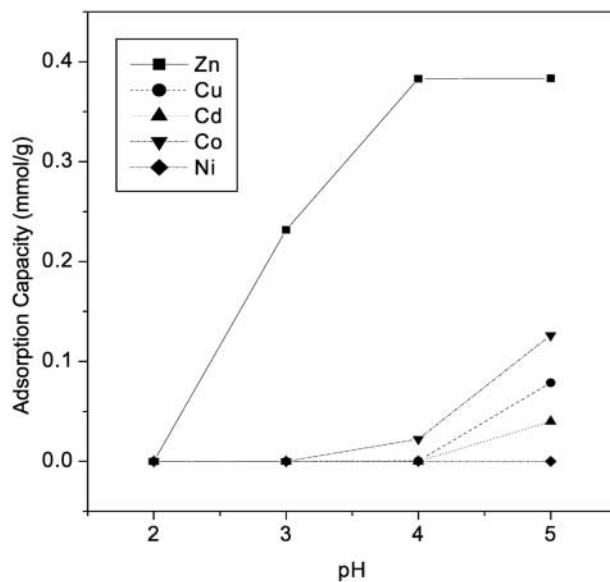


Figure 3. Adsorption capacity of heavy metal ions as a function of pH: SPDC 0.2 g, heavy metal ion solution 5 mmol/L; 25 mL.

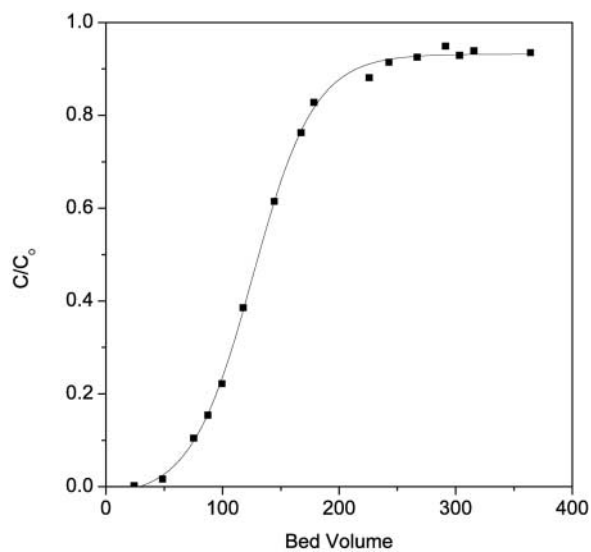


Figure 4. Break-through curve for zinc ions using SPDC: feed solution 1 mmol/L; pH 4.3; flow rate 5 mL/min, SPDC 5 g, bed diameter 16 mm.



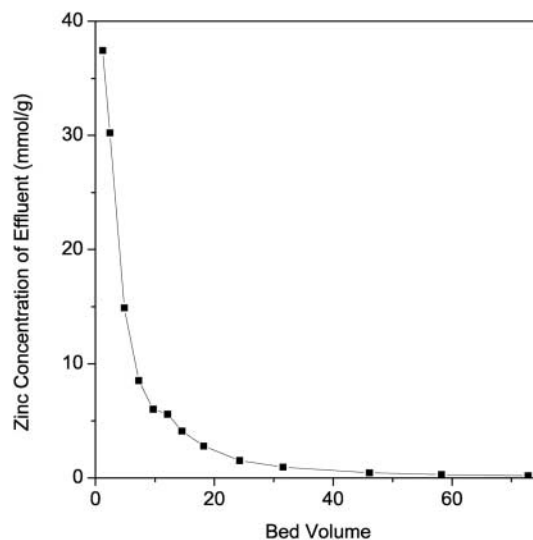


Figure 5. Elution of zinc ions using SPDC: elution solution 0.1 M HCl; flow rate 5 mL/min, SPDC 5 g, bed diameter 16 mm.

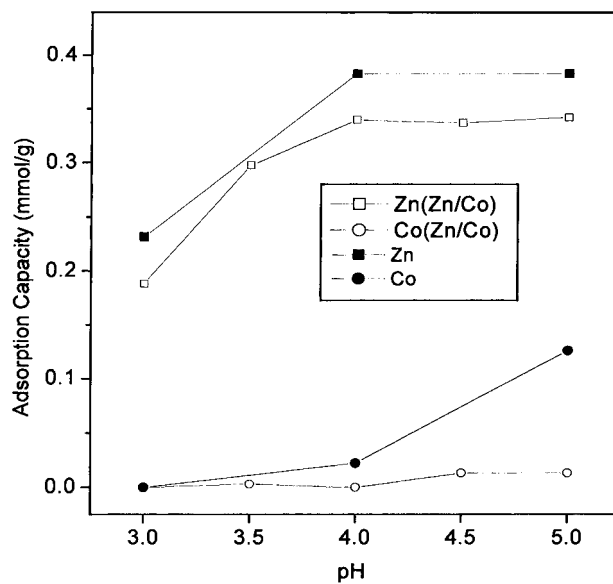


Figure 6. Comparison of adsorption capacity for zinc and cobalt for a single and binary solution: SPDC 0.2 g, heavy metal solution 5 mmol/L; 25 mL.



1 ppm of zinc ion in the effluent. The zinc concentration in the effluent increased up to the saturation point after 300 bed volumes.

The elution of zinc ions from the sample after performing the break-through experiment was also studied. A solution of 0.1 M HCl was passed through the bed at a rate of 5 mL/min. As shown in Fig. 5, the zinc concentration of the effluent was initially very high and then decreased dramatically within 40 bed volumes. This result indicates that the rate of elution is faster than that of adsorption. Ninety percent of the zinc ions were eluted in up to 30 bed volumes.

Separation of Zinc Ion from Binary Solution

The adsorption capacity of metal ions in single and binary solution containing Zn^{2+} and Co^{2+} were compared, as shown in Fig. 6. The adsorption capability for zinc ion increased with pH from a solution pH of 3–4 and remained constant for pH values from 4 to 5. Compared with adsorption capacities in single solution, the absolute adsorption capacities for both zinc and cobalt ion decreased. However, the relative capacity, the selectivity of zinc ion for cobalt

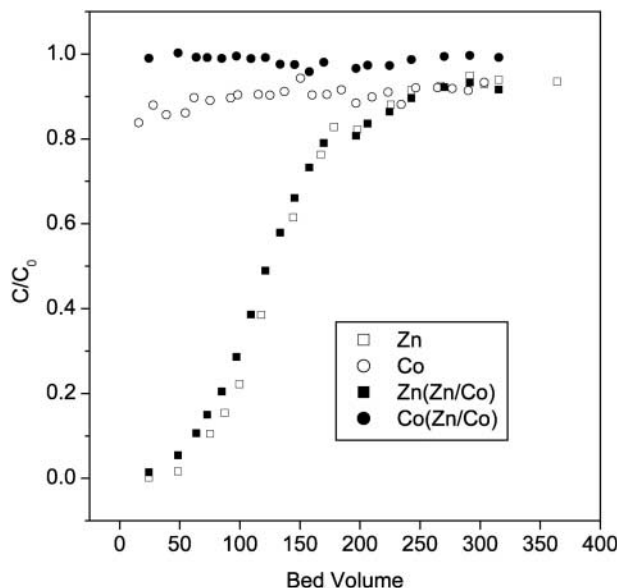


Figure 7. Break-through curves for zinc and cobalt ions for single and binary solutions: Feed solution 1 mmol/L; pH 4.0; flow rate 5 mL/min, SPDC 5 g, bed diameter: 16 mm.



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ion increased by more than two times. This indicates that the presence of zinc ion seriously interfered with adsorption of cobalt ions. This can be explained by the competitive adsorption of the two metal ions. These results suggested that the optimum pH for quantitative and selective separation of zinc ion from cobalt is approximately 4–5 without precipitation.

The zinc selectivity of the SPDC over cobalt in a continuous system was also investigated using a fixed bed reactor. Figure 7 shows the break-through curves for a binary solution containing Zn^{2+} and Co^{2+} . Approximately 30 bed volumes of feed solution can be passed through, while maintaining the zinc concentration below 1.0 ppm in the effluent. This value is smaller than that in the case of extraction of the single zinc solution (50 bed volumes). The zinc concentration in the effluent increased and the adsorbent reached saturation after approximately 300 bed volumes. Cobalt ion was not adsorbed as shown in the figure. The effluent pH increased from 2.9 at 25 bed volumes to 3.9 at 316 bed volumes. The change in pH of the aqueous solution reflects the adsorption of zinc ion to the adsorbent.

These results indicate that zinc ion, which has relatively high affinity for CYANEX 272, suppresses the adsorption of cobalt ion. In addition, the selective

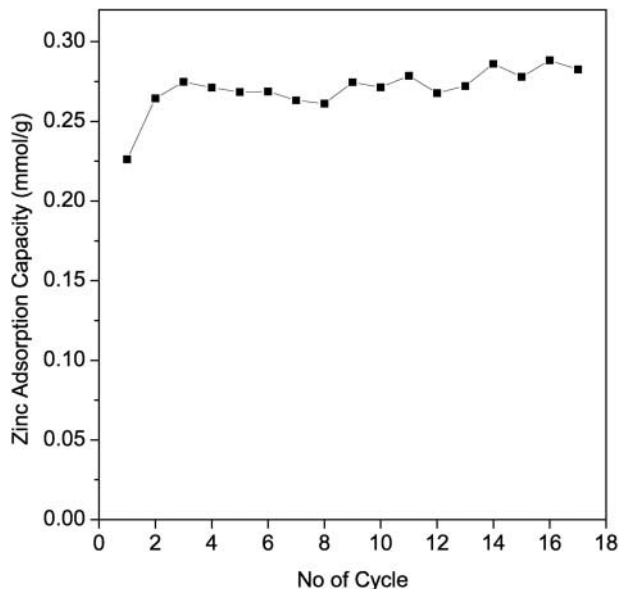


Figure 8. Successive adsorption–elution of SPDC: SPDC 0.5 g, zinc solution 2 mmol/L; 200 mL; pH 4.0, elution solution 0.1 M HCl; 100 mL, adsorption operation time 2 hr, desorption operation time 3 hr.



and quantitative removal of zinc ion from Cu^{2+} , Cd^{2+} , and Ni^{2+} using a fixed-bed reactor would be possible, providing the inlet solution pH is controlled at approximately 4.

Regeneration

Figure 8 shows the change in zinc-adsorption capacity during successive operations. The adsorption capacity increased from 0.226 mmol/g for the first operation to around 0.27 mmol/g for later ones. The initial low adsorption capacity may be explained by the low adsorption rate or short contact time, which is likely due to surface hydrophobicity. It was also observed that the successive use of the SPDC with acidic treatment slightly increases the adsorption rate. However, the adsorption capacities after regeneration were less than those shown in Fig. 3. Although a zinc solution at pH 4 was fed to the reactor, the pH of the column was decreased to around 3.5 owing to the effect of 0.1 M HCl during the elution. This caused a decrease in Zn adsorption to 0.27 mmol/g, corresponding to the capacity depicted in Fig. 3. These results indicate that the SPDC is regenerable and efficient in terms of cyclic use.

CONCLUSIONS

Di-2,4,-trimethylpentyl phosphinic acid was immobilized on the surface of silica supports after surface silanization with dichlorodimethylsilane and chlorotripropylsilane. Significant pores were retained after silanization and allowed for the impregnation of CYANEX 272. The CYANEX 272 is believed to attach to the silanized surface by hydrophobic attractions, such as van der Waals forces. The resulting adsorbents showed excellent stability under acidic conditions. The order of adsorption capacity of SPDC was $\text{Zn}^{2+} > \text{Co}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} \gg \text{Ni}^{2+}$ under the conditions ($< \text{pH } 5$) used in this study. Break-through and elution studies show that SPDC can be used effectively for the removal of zinc ions in a fixed-bed operation. The selective and quantitative removal of zinc ion from Co^{2+} was possible at solution pH of 4, and this can be extended to a binary system containing Zn^{2+} and one among Cu^{2+} , Cd^{2+} , and Ni^{2+} . Adsorbed zinc ions could be recovered by treatment with an acidic solution, and thus permitting cyclic use after regeneration.

In conclusion, the possibility of separating zinc ions from an aqueous solution using modified silica was clearly demonstrated in this paper, and more practical research is proceeding using actual wastewater to test this application for practical processes.



SYMBOLS

| | |
|------------|--|
| CYANEX 272 | Di-2,4,4-trimethylpentyl phosphinic acid |
| SP | Silica powder |
| SPC | SP silanized with chlorotripropylsilane |
| SPCC | SPC impregnated with CYANEX 272 |
| SPD | SP silanized with dichlorodimethylsilane |
| SPDC | SPD impregnated with CYANEX 272 |
| SPDCM | Metal-adsorbed SPDC |

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